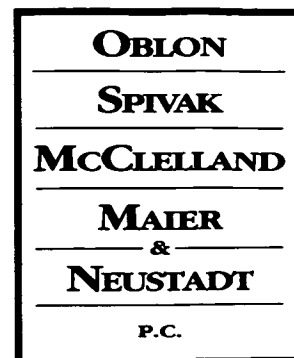




Docket No.: 201940US-25

ASSISTANT COMMISSIONER FOR PATENTS
WASHINGTON, D.C. 20231



ATTORNEYS AT LAW

CHARLES L. GHOLZ
(703) 412-6485
CGHOLZ@OBLON.COM

RE: Application Serial No.: 09/805,997
Applicants: Jeffrey R. MOUNT, et al.
Filing Date: MARCH 15, 2001
For: METHOD AND SYSTEM...
Group Art Unit: 2162
Examiner: UNASSIGNED

RECEIVED

JUN 28 2001

SIR:

Technology Center 2100

Attached hereto for filing are the following papers:

**LETTER TO THE OFFICIAL DRAFTSMAN
SUBSTITUTE FORMAL DRAWINGS (7 SHEETS)**

Our check in the amount of -0- is attached covering any required fees. In the event variance exists between the amount enclosed and the Patent Office charges for filing the above-noted documents, including any fees required under 37 C.F.R. 1.136 for any necessary Extension of Time to make the filing of the attached documents timely, please charge or credit the difference to our Deposit Account No. 15-0030. Further, if these papers are not considered timely filed, then a petition is hereby made under 37 C.F.R. 1.136 for the necessary extension of time. A duplicate copy of this sheet is enclosed.

Respectfully submitted,

OBLON, SPIVAK, McCLELLAND,
MAIER & NEUSTADT, P.C.

Charles L. Gholz
Attorney of Record
Registration No. 26,395

Joseph A. Scafetta, Jr.
Registration No. 26,803



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(703) 413-3000 (phone)

(703) 413-2220 (fax)

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JUN 28 2001
Technology Center 2100

Docket No.: 201940US-25

IN THE UNITED STATES PATENT & TRADEMARK OFFICE

IN RE APPLICATION OF: :
Jeffrey R. MOUNT, et al. : GROUP ART UNIT: 2162
SERIAL NO: 09/805,997 :
FILED: MARCH 15, 2001 : EXAMINER: UNASSIGNED
FOR: METHOD AND SYSTEM
FOR ACCUMULATING
COUPON VALUES...

LETTER TO THE OFFICIAL DRAFTSMAN

ASSISTANT COMMISSIONER FOR PATENTS
WASHINGTON, DC 20231

SIR:

Attached hereto please find 7 sheets of Substitute Formal Drawings. It is requested that the enclosed 7 sheets of Substitute Formal Drawings be entered to replace the drawings previously filed in this application.

Respectfully submitted,

OBLON, SPIVAK, McCLELLAND,
MAIER & NEUSTADT, P.C.

Joseph A. Scafetta Jr.

Charles L. Gholz
Registration No: 26,395
Attorney of Record

Joseph A. Scafetta, Jr.
Registration No. 26,803



22850

Tel.: (703) 413-3000
Fax #: (703) 413-2220

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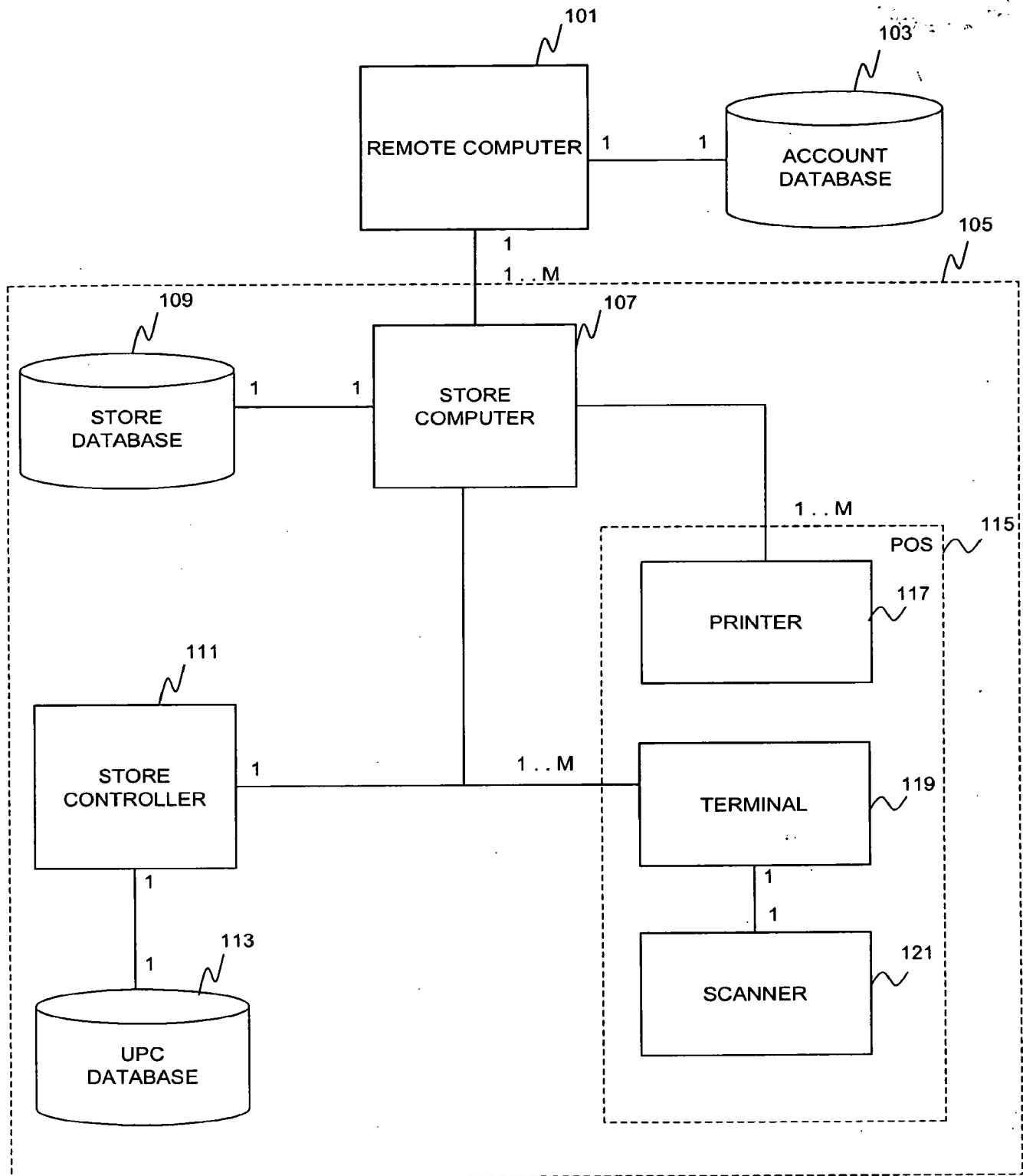


FIG. 1

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CID	ACCOUNT ID

FIG. 2A

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CID	ACCOUNT ID	AMOUNT	DATE

FIG. 2B

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ACCOUNT ID	PERIOD TOTAL

FIG. 2C

216

218

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ACCOUNT ID	ACCOUNT TOTAL

FIG. 2D

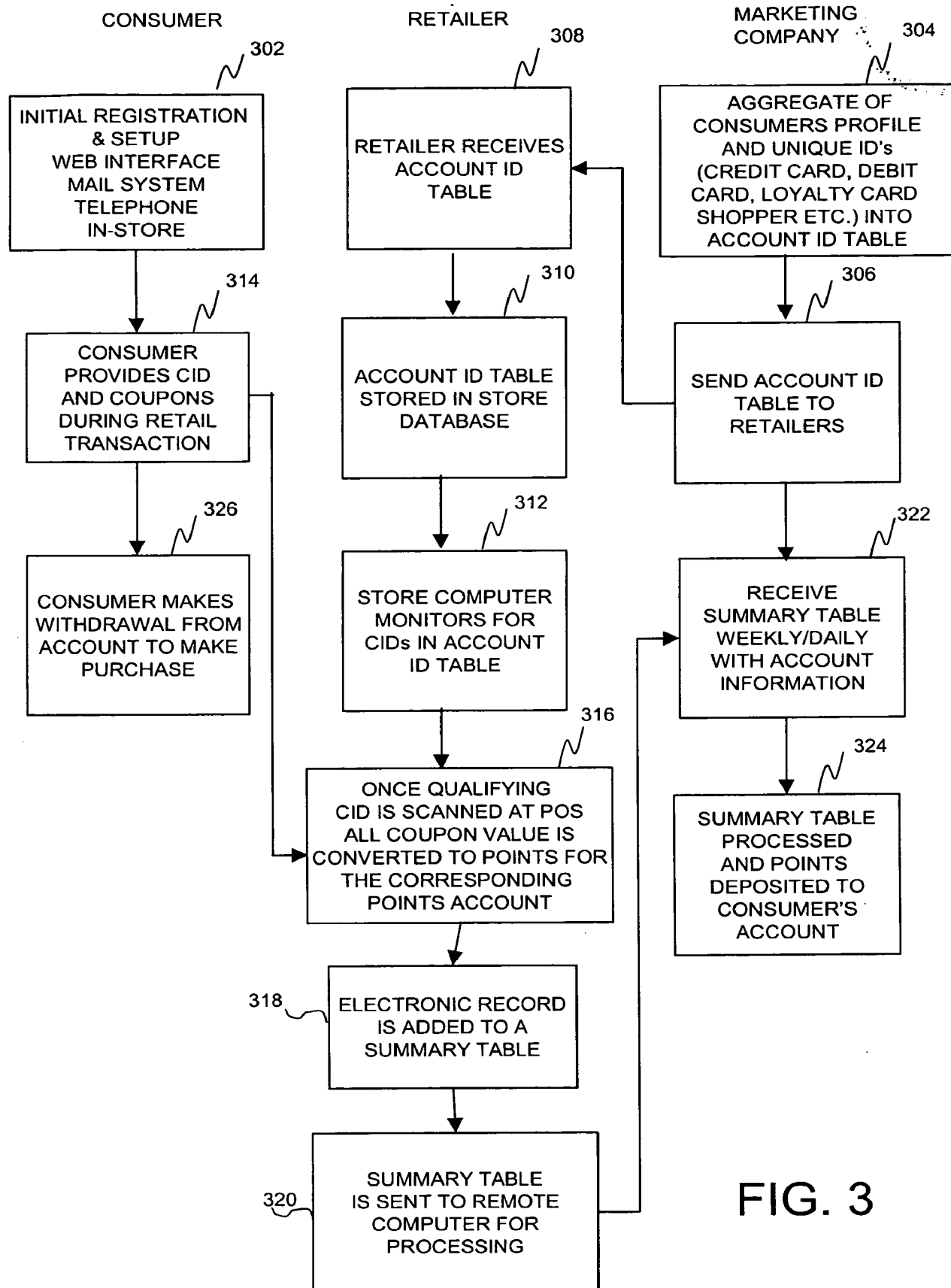


FIG. 3

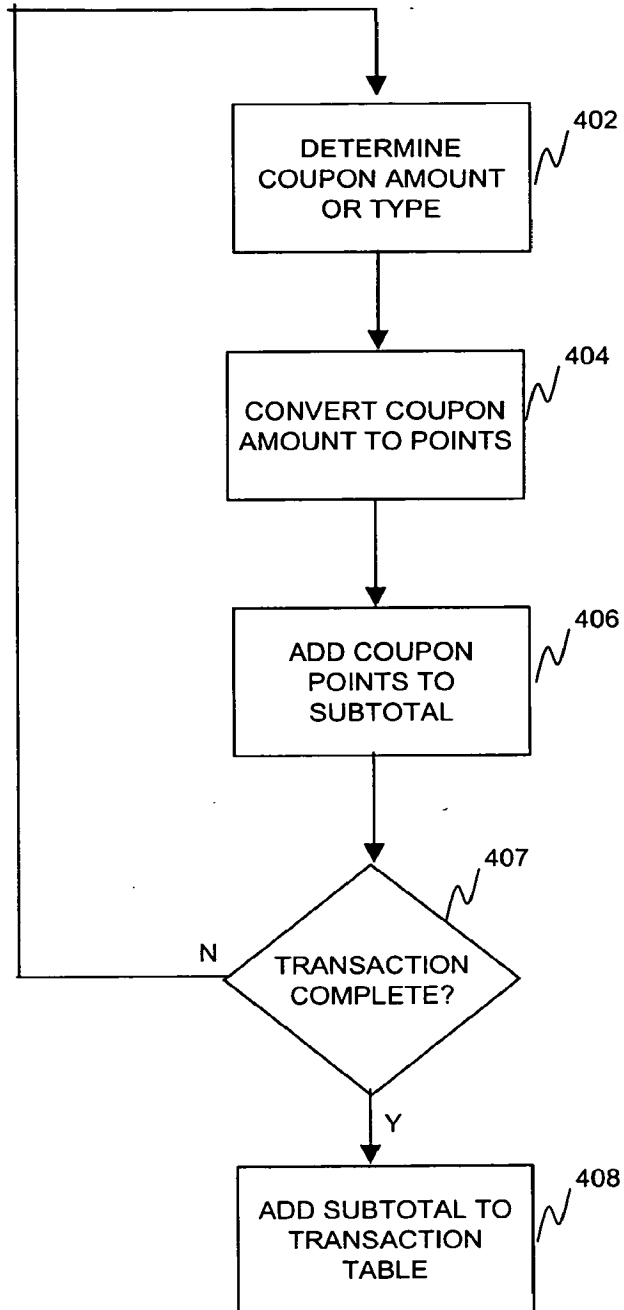


FIG. 4

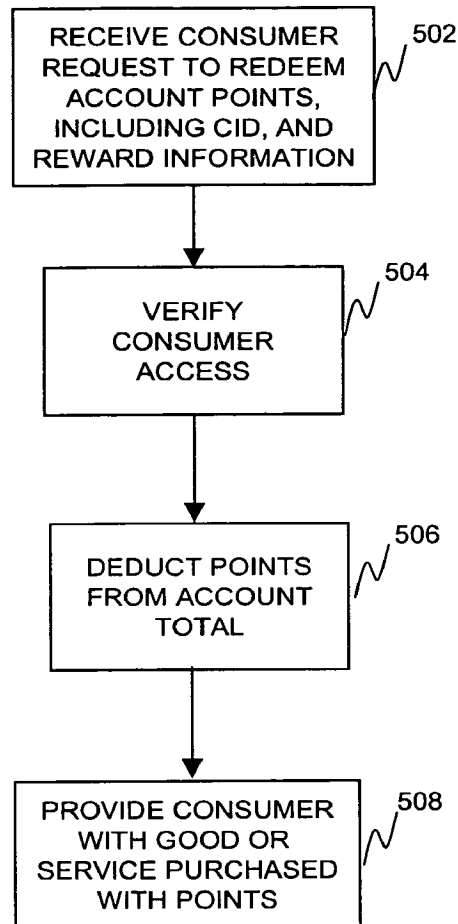
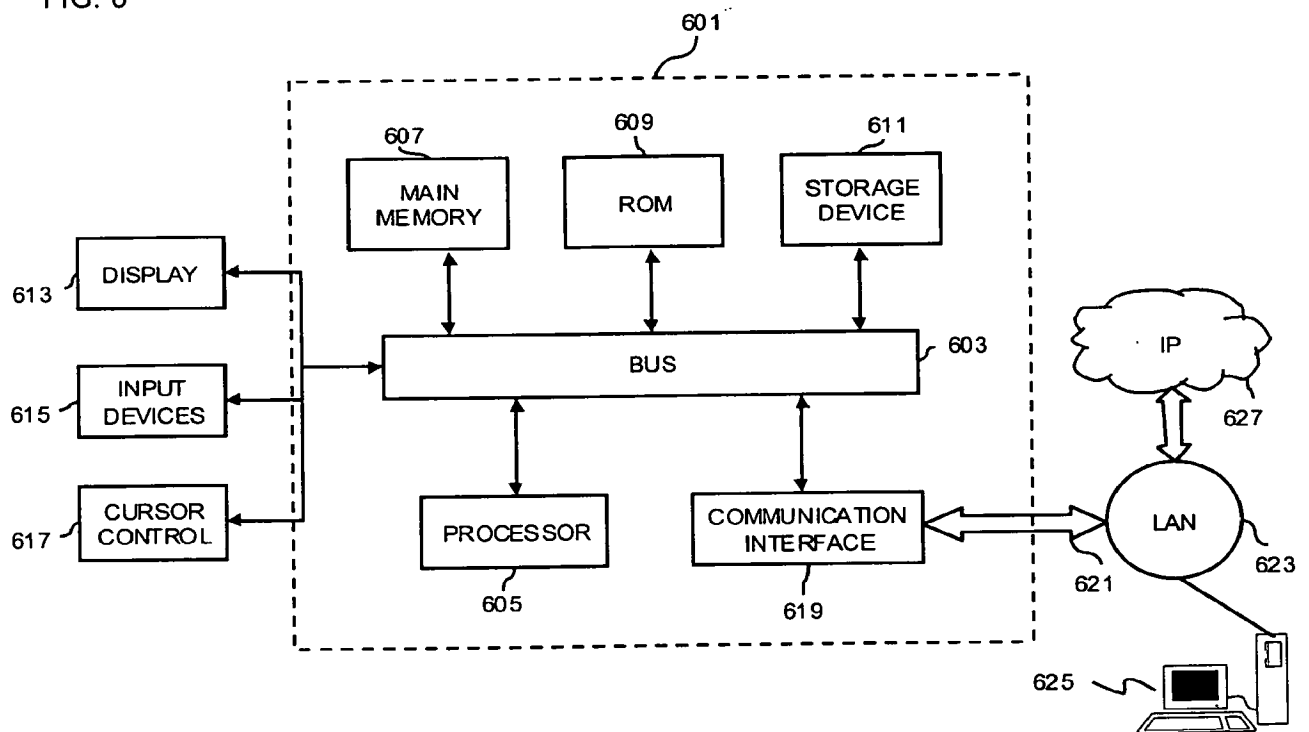


FIG. 5

FIG. 6



- 8 -

carboxylic acid amide (4.94 g; 25.6 mmol), sodium nitrite (4.4 g; 64 mmol) and isopropyl acetate (40 ml) were charged. The mixture was kept under mechanic stirring and heated at 50°C. In one portion iodine (1.9 g; 7.5 mmol) and then, in 3 hours, Oxistrong 15[®] (6 ml) were added. At the end of the addition the reaction mixture was kept under stirring for 1 hour and cooled to 20°C. After addition of water (30 ml), the mixture was further cooled at 5°C for 1 hour. The solid was filtered and washed with isopropyl acetate (3x10 ml), pre-cooled at 0°C, and with water (2x10 ml). After drying in oven under vacuum at 50°C overnight, 8-fluoro-3-nitro-2*H*-chromene-5-carboxylic acid amide (4.7 g; HPLC titre 90%; 70% yield) was obtained. The mother liquors of the reaction were treated with a 15% solution of sodium metabisulphite (20 ml) up to decoloration. The phases were separated, the organic phase was dried and the organic solvent was removed under reduced pressure obtaining a solid (0.8 g) containing 49% of 8-fluoro-3-nitro-2*H*-chromene-5-carboxylic acid amide. Overall yield: 76.4%.

Example 3

Preparation of 8-fluoro-3-nitro-2*H*-chromene-5-carboxylic acid amide

Into a reactor, equipped with a mechanic stirrer and a reflux condenser, 8-fluoro-2*H*-chromene-5-carboxylic acid amide (3.1 g; 15 mmol), sodium nitrite (3.1 g; 45 mmol) and toluene (30 ml) were charged at room temperature and under inert gas. The mixture was heated under stirring at 50°C, then iodine (1.9 g; 7.5 mmol) and, slowly in 4 hours, Oxistrong 15[®] (3.7 ml) were added. At the end of the addition the reaction mixture was kept under stirring for a further hour, then cooled to 0°C. A 20% solution of sodium metabisulphite (about 15 ml) was added and the mixture was kept under stirring for 1 hour. After filtration the solid was washed with water (2x10 ml) and with toluene (10 ml) and dried in oven under vacuum at 50°C overnight obtaining 8-fluoro-3-nitro-2*H*-chromene-5-carboxylic acid amide (3.4 g; titre 78%; 74% yield).

Example 4

Preparation of 8-fluoro-3-nitro-2*H*-chromene-5-carboxylic acid methyl ester

Into a reactor, equipped with mechanic stirrer and reflux condenser, 8-fluoro-2*H*-chromene-5-carboxylic acid methyl ester (6.6 g; 30 mmol), sodium nitrite (6.2 g; 90 mmol) and ethyl

- 9 -

acetate (60 ml) were added at room temperature and under inert gas. The mixture was heated under stirring at 50°C, then iodine (2.6 g; 10 mmoles) and, slowly in 4 hours, Oxistrong 15[®] (7.4 ml) were added. At the end of the addition the reaction mixture was kept under stirring for a further hour, then cooled at 0°C. A 20% solution of sodium metabisulphite (about 25 ml) was added and the mixture was kept under stirring for 1 hour. After filtration the solid was washed with water (2x10 ml). The mother liquors were separated and, the previously filtered solid was added to the organic phase. The solvent was removed under reduced pressure and the semisolid residue was taken up with methanol (about 10 ml) and kept under stirring at 0°C for 1 hour. After filtration and wash of the panel with methanol pre-cooled at 0°C (3 ml), the resultant solid was dried in oven under vacuum at 40°C overnight obtaining 8-fluoro-3-nitro-2H-chromene-5-carboxylic acid methyl ester (4.6 g; titre 92%; 55% yield). The mother liquors were evaporated to dryness obtaining an oil (2.7 g) containing 55% of 8-fluoro-3-nitro-2H-chromene-5-carboxylic acid methyl ester. Overall yield 75%.

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Example 5

Preparation of 8-fluoro-3-nitro-2H-chromene-5-carboxylic acid amide

Into a reactor, equipped with a mechanic stirrer and a reflux condenser, 8-fluoro-2H-chromene-5-carboxylic acid amide (2 g; 10 mmoles), sodium nitrite (1.4 g; 20 mmoles), potassium iodide (0.33 g; 2 mmoles) and ethyl acetate (20 ml) were charged at room temperature and under inert gas. The mixture was heated at 40°C, then Oxistrong 15[®] (4 ml) was added in 4 hours. At the end of the addition the reaction mixture was kept under stirring for 1.5 hours, then cooled at 20°C and diluted with ethyl acetate up to complete dissolution (about 150 ml). After washing with a 20% sodium metabisulphite solution, the phases were separated. The organic phase was washed with a saturated sodium chloride solution, dried and the solvent was removed under reduced pressure, obtaining 8-fluoro-3-nitro-2H-chromene-5-carboxylic acid amide (1.8 g; titre 88%; 66% yield).

25

Example 6

Preparation of 8-fluoro-3-nitro-2H-chromene-5-carboxylic acid amide

Into a reactor, equipped with a mechanic stirrer and a reflux condenser, 8-fluoro-2H-chromene-5-carboxylic acid amide (120 g; 0.609 moles), sodium nitrite (96.6 g; 1.4 moles),

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- 10 -

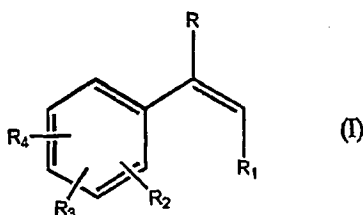
iodine (31.2 g; 0.123 moles) and ethyl acetate (720 ml) were charged at room temperature and under inert gas. The mixture was heated under stirring at 40°C, then Oxistrong 15[®] (173.4 g) was added in 4 hours. At the end of the addition the reaction mixture was kept under stirring
5 for 1 hour, then cooled at 20°C. Water (480 ml) was added and the mixture was kept under stirring for 1 hour. After filtration and wash of the panel with isopropyl acetate pre-cooled at 0°C (2x120 ml) and then with water (150 ml), the solid was dried in oven under vacuum at 50°C overnight obtaining 8-fluoro-3-nitro-2*H*-chromene-5-carboxylic acid amide (112.7 g; titre 91%; 70% yield).

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Claims

- 1) A process for the nitration of conjugated alkenes of formula

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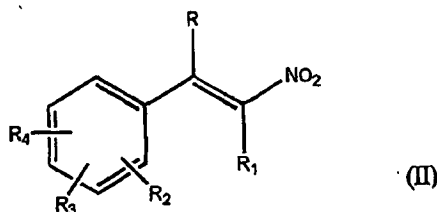


wherein

- R is a hydrogen atom, an optionally substituted phenyl, a linear or branched C₁-C₄ alkyl; R₁ is a hydrogen atom or a linear or branched C₁-C₄ alkyl, optionally substituted by an OH or C₁-C₄ alkoxy group; R₂, R₃ and R₄, the same or different, are selected among hydrogen and halogen atoms, linear or branched C₁-C₄ alkyl or alkoxy groups, carboxylic groups, aminocarbonyl groups, alkoxycarbonyl, alkylcarbonyl, mono- or di-alkylaminocarbonyl, alkylcarbonylamino and alkylcarbonyloxy groups having from 1 to 4 carbon atoms in the alkyl moiety; or two of R₂, R₃ and R₄, in ortho between them, form a methylenedioxy group; or R₁ together with R₂ forms a cyclic system with 5-7 terms condensed with the aromatic ring and optionally containing an oxygen atom; or R₁ together with R forms a cyclic system with 5-7 terms;

which allows to obtain β-nitro-alkenes of formula

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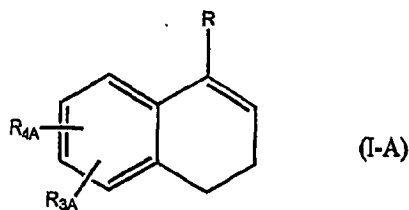


- 25 wherein R, R₁, R₂, R₃ and R₄ have the already reported meanings; characterised in that the nitrating agent is a mixture of an inorganic nitrite and iodine in the presence of an oxidising agent.
- 2) A process according to claim 1 wherein the iodine is in an amount from 0.1 to 0.8 moles per mole of the compound of formula I.
- 30 3) A process according to claim 1 wherein the inorganic nitrite is selected among silver

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nitrite, sodium nitrite and potassium nitrite.

- 4) A process according to claim 3 wherein the inorganic nitrite is sodium nitrite.
- 5) A process according to claim 1 wherein the inorganic nitrite is in an amount from 2 to 4 moles per mole of the compound of formula I.
- 6) A process according to claim 1 wherein the oxidant agent is selected among peracids, oxygen peroxide and inorganic nitrites.
- 7) A process according to claim 6 wherein the oxidant agent is a mixture of peracetic acid, oxygen peroxide and water.
- 8) A process according to claim 1 wherein the iodine is formed *in situ* from alkaline iodides.
- 9) A process according to claim 1 wherein the temperature is from 40°C to 50°C.
- 10) A process according to claim 1 for the nitration of styrenes, optionally substituted on the aromatic ring by from 1 to 3 methoxy groups or by a methylenedioxy group.
- 11) A process according to claim 1 for the nitration of dihydronaphthalenes, optionally substituted by methoxy, methyl, ethyl, fluoro, chloro, bromo, iodo, carboxy, methoxycarbonyl groups or by a methylenedioxy group.
- 12) A process according to claim 11 for the nitration of dihydronaphthalenes of formula



wherein

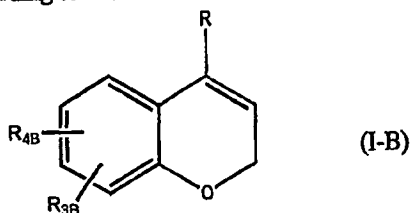
- 25 R_{3A} and R_{4A} , the same or different, are hydrogen atoms, methoxy, methyl, ethyl, fluoro, chloro, bromo, iodo, carboxy, methoxycarbonyl groups or, together, form a methylenedioxy group;
- R is a hydrogen atom, an optionally substituted phenyl, a linear or branched C_1 - C_4 alkyl.
- 13) A process according to claim 1 for the nitration of benzopyranes optionally substituted
- 30 by methoxy, methyl, ethyl, fluoro, chloro, bromo, iodo, carboxy, methoxycarbonyl,

- 13 -

aminocarbonyl or methylaminocarbonyl groups.

14) A process according to claim 13 for the nitration of the benzopyrans of formula

5



wherein

10 R_{3B} and R_{4B} , the same or different, are hydrogen atoms, methoxy, methyl, ethyl, fluoro, chloro, bromo, iodo, carboxy, methoxycarbonyl, aminocarbonyl or methylaminocarbonyl groups;

R is a hydrogen atom, an optionally substituted phenyl, a linear or branched C_1 - C_4 alkyl.

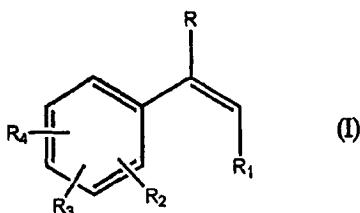
15) A process according to claim 13 for the nitration of the compound 8-fluoro-2H-chromene-5-carboxylic acid amide.

- 14 -

Abstract

A process for the nitration of conjugated alkenes of formula

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wherein R , R_1 , R_2 , R_3 and R_4 have the meanings reported in the description, which allows to obtain the corresponding β -nitro-alkenes, characterised in that the nitrating agent is a mixture of an inorganic nitrite and iodine in the presence of an oxidising agent is described.